電気材料技術雑誌 第14巻第2号
J.Soc.Elect.Mat.Eng. Vol.14, No.2, 2005

Polymerizable Macrocyclic Molecules as Unique Host Matrix for Lanthanide Complexes

Rahmat Hidayat[1], Okihiro Sugihara[1], Masaaki Tsuchimori[2], Manabu Kagami[2], Tadatomi Nishikubo[3], Toshikuni Kaino[1]

[1]*Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan*
E-mail: rahmat_h@tagen.tohoku.ac.jp
[2]*Toyota Central R&D Labs. Inc., 41-1 Yokomichi, Nagakute, Aichi-Gun, Aichi, Japan.*
[3]*Department of Applied Chemistry, Faculty of Engineering, Kanagawa University, Rokkakubashi, Kanagawa-Ku, Yokohama, Japan*

Lanthanide ions are used for wide variety of applications, such as lasers in optical communication and molecular sensing in biosciences. Lanthanide ions are commonly soluble in aqueous solution and ionic glassy materials, but they are poorly soluble in organic and polymer materials. In order to increase their solubility in organic solvents and polymer, lanthanide ions are usually complexed with small ligand molecules, such as β-diketones, pyridine and bipyridine.[1] Study on complexation and optical properties of lanthanide ions with macromolecules having macrocylic or cavitand shape such as crown ethers, cryptands, calixarenes and polydentate hemisperands have been much also reported.[2-5] Furthermore, when energy transfer from ligand to lanthanide ion is highly efficient, the ligand molecules may perform a function of light antenna that absorb photon and then transferred the energy to lanthanide ions. Following the progress in polymer optical fiber and planar waveguide development, the incorporation of lanthanide ions into organic polymers has been increasingly studied. There are numerous reports related to this effort, such as doping the ions into organic polymers, organically modified silicate (ORMOSIL) matrices, and silica based host materials.[6-8]

Recently, polymerizable macrocyclic molecules based on calixarene and calixresorcinarene molecules have been developed.[9] These macrocyclics have acrylate or epoxy groups attached to their lower or upper rims. Calixarene acrylates shows high transparency in visible and near-infra red region, so they are also applicable for optical waveguide devices. Fabrication of calixarene acrylate waveguides by means of one- and two-photon polymerization techniques has been also demonstrated.[10] We are presently interested in developing active optical waveguides based on these macrocyclic polymers which are doped with lanthanide complexes. In the present work, we investigated the incorporation of europium complexes into macrocylic polymers. In most cases, aggregation of lanthanide complex in polymer could be a serious problem hindering its utilization at high doping. Here, it important to clarify the interaction between lanthanide ions and macrocylic monomer. In a situation when an interaction between lanthanide ions and macrocylic monomers are established, either by coordination bond formation or inclusion phenomenon, the ions will be completely separated from each other. As a result, even at high doping concentration, complex aggregation and interaction between neighboring ions would be suppressed.

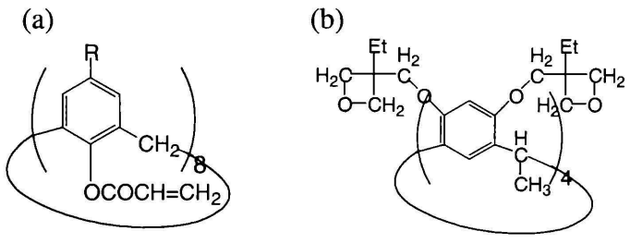

Fig. 1 Molecular structure of (a) BUCA[8]Ac with R=*t*-Bu and BOCA[8]Ac with R=*t*-Bu and *t*-Oc, and (b) CRA[4]Ox

Figure 1 shows the molecular structure of macrocyclic monomers used in the present work. BUCA[8]Ac and BOCA[8]Ac were received from Shin Nakamura Chemical Co., Ltd. and previously purified prior to use. BOCA[8]Ac is more soluble in common organic solvent and acrylate monomers than BUCA[8]Ac. For representative of lanthanide complex in this work, Europium (III) ion complexed with dibenzoylmethane (DBM) was chosen. It is prepared by means of deprotonation in a similar method reported in literature, but the concentration of deprotonation agent (NaOH) and ligand DBM was reduced in comparison to $EuCl_3$ in order to form partial complexation. Eu(DBM) complex was mixed with those macrocyclic monomers in dichloromethane, and subsequently followed by reprecipitation in ethanol. Thin film and bulk polymers containing these mixtures were prepared by thermal polymerization with addition of acrylate monomers as diluter. Photoinitiators, i.e. BDK or TPO, have been used for and for photopolymerization, whereas thermal initiator AIBN has been used for thermal polymerization. Since the oxetane groups were not polymerized by radical polymerization, while the complex were decomposed by cationic polymerization, Eu(DBM)/CRA[4]Ox was then embedded in acrylate polymer matrix.

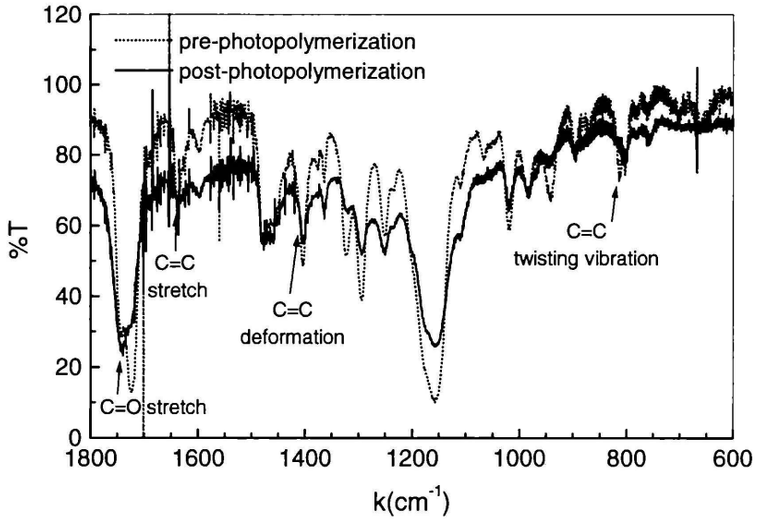

Fig. 2 FTIR spectra of BOCA[8]Ac with two-functional acrylate as diluter before (dot line) and after (solid line) polymerization.

In order to clarify that the acrylate groups are polymerized, FTIR spectra before and after polymerization were measured. Here, since thin film samples are more suitable for the measurement, thin film samples were prepared by photopolymerization on the top of silicon wafer as substrate. FTIR spectra in Fig. 2 shows the reduction of absorption assigned to C=C vibrations, i.e. C=C stretching at 1640 cm^{-1}, C=C deformation at 1410 cm^{-1} and C=C twisting at 820 cm^{-1}. This result indicates the conversion of C=C bond in acrylate groups into C–C bond by the polymerization.

The absorption spectrum of dilute solution Eu(DBM) shows intense broad band with absorption peak at 340 nm and absorption tail at around 410nm. There is no significant change on this absorption band when the complex was mixed with BOCA[8]Ac and CRA[4]Ox, indicating that electronic states of the complex is not significantly affected. The NMR spectrum of Eu(DBM)/BOCA[8]Ac shows merely an overlap of BOCA[8]Ac and Eu(DBM) spectra, indicating only random distribution of the ions without any interaction with BOCA[8]Ac. On the contrary, the NMR spectrum of Eu(DBM)/CRA[4]Ox is significantly different from that of pure CRA[4]Ox, which is indicated by down-field shifting of proton chemical shift (δ_H) of about 1 ppm from ca. 3.7 ppm to ca. 4.7 ppm (indicated by * in Fig. 3). These chemical shifts are originated from protons (^1H) at methane groups adjacent to resorcinarene oxygen atoms. The shifting ($\Delta\delta_H$) is relatively small which is corresponding to dipolar or pseudocontact shift induced by paramagnetism properties of Eu(III) ions. This fact indicates the complexation of the non-covalent coordination bond between calixresorcinarenes and Eu(III) ions in the outer of the first coordination sphere.

Figure 4 shows the emission spectra of Eu(DBM) in acrylate polymers and Eu(DBM)/CRA[4]Ox in BOCA[8]Ac/acrylate polymers. The spectra show intense hypersensitive peak ($^5D_0 \rightarrow {}^7F_2$) in comparison to other peaks, which is typical emission characteristic of europium complexes with a disordered square antiprism coordination structure. The spectrum of Eu(DBM)/CRA[4]Ox is broader consisting of perceptible three peaks in comparison to the other

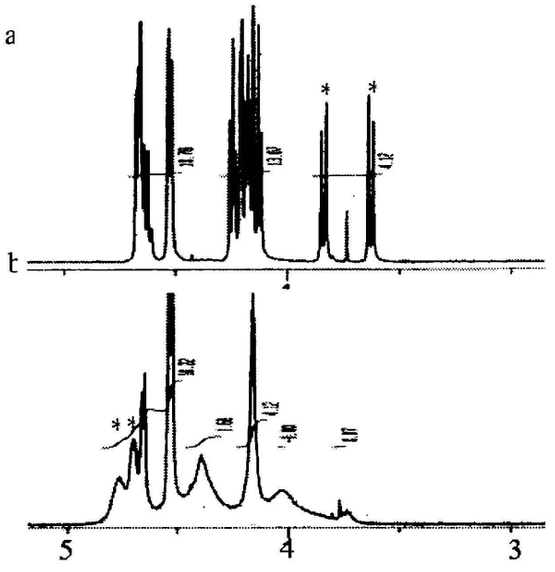

Fig. 3 NMR spectra of (a) pure CRA[4]Ox and (b) mixture of Eu(DBM)/CRA[4]Ox in $CDCl_3$.

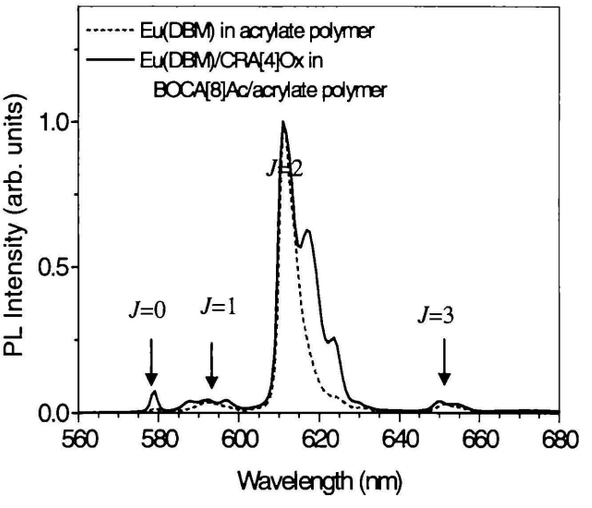

Fig. 4 Fluorescence spectra of Eu(DBM) and Eu(DBM)/CRA[4]Ox in two functional BOCA[8]Ac/acrylate polymers.

spectrum. This broadening is attributed to Stark splitting due to the change of ligand field induced by a small alteration in its coordination structure.

In summary, complexation of europium ions with polymerizable macrocyclic molecules has been observed in Eu(DBM)/CRA[4]Ox mixture. The complexation has been clarified by employing emission and NMR spectroscopies in conjunction. This unique complexation with polymerizable macrocyclic molecules could be useful for developing optically active devices based on lanthanide-doped polymers in the future.

REFERENCES

1. G. Vicentini *et al.*, Coord. Chem. Rev. **196** (2000) 353; C. R. De Silva *et al.*, Inorg. Chim. Acta **357** (2004) 630.
2. S. S. Braga *et al.*, J. Phys. Chem. B **106** (2002) 11430-11437.
3. R. Reisfeld *et al.*, Optical Materials **24** (2003) 1
4. L. H. Slooff *et al.*, J. Appl. Phys. **91** (2002) 3955.
5. *Calixarenes: A Versatile Class of Macrocyclic Compounds*; J. Vicens and V. Bohmer (Eds.), (Kluwer Ac. Publ., 1991, Dordrecht)
6. K. Kurikiri, Y. Koike and Y. Okamoto, Chem. Rev. **102** (2002) 2347
7. E. J. Nassar *et al.*, Mat. Res., **4** (2001) 18-22; E. J. Nassar, O. A. Serra, and I. L. V. Rosa, J. Alloys Comp., **250** (1997) 380.
8. X. Fan *et al.*, **58** (2004) 2217.
9. T. Nishikubo *et al.*, Polym. Journal, **35** (2003) 213.
10. Y. Yamagishi *et al.*, Proc. SPIE **4991** (2003) 414; K. Komatsu *et al.*, Polym. Preprints - Japan, **53** (2004) 4583.